Characterization Studies of High Capacity Composite Electrode Structures

Principal Investigators: Michael Thackeray and Jason Croy

Chemical Sciences and Engineering Division

Argonne National Laboratory

Annual Merit Review

DOE Vehicle Technologies Program

Washington, DC

5-9 June, 2017

ES235

Overview

Timeline

- Start date: FY16
- End date: FY18
- Percent complete: 50%

Budget

- Total project funding: 100% DOE
- FY16 Funding:

  Characterization/Modeling: $500K

Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

Partners

- Lead PI: Michael Thackeray, Co-PI: Jason Croy
- Collaborators:
  - CSE, Argonne: Eungje Lee, *Joong Sun Park*, Arturo Gutierrez, *Bryan Yonemoto*, Meinan He, Roy Benedek, Fulya Dogan (NMR)
  - APS, Argonne: Mali Balasubramanian (XAS), Yang Ren (HRXRD, ND)
  - ES, Argonne: Youngho Shin, Ozge Kahvecioglu Feridun, Greg Krumdick
  - MSD, Argonne: Hakim Iddir
  - Northwestern University, NUANCE: Vinayak Dravid, Jinsong Wu (TEM), Soo Kim, Chris Wolverton
  - PNNL: Chongmin Wang, Pengfei Yan (TEM)
  - ORNL: Harry Meyer & Rose Ruther (XPS), Ashfia Huq (ND)
  - Rutherford Appleton Lab (ISIS): Bill David (ND)
  - Industry: Argonne licensees and collaborators

Objectives

- Explore the fundamental, atomic-scale processes that are most relevant to the challenges of next-generation, structurally-integrated electrode materials, in particular:
  - Understanding, via characterization and modeling, the atomic-scale processes of promising, end-member spinel components
  - Characterization, modeling, and design of surfaces that enable stable cycling of lithium- and manganese-rich compositions
  - Improving the structural design, composition and electrochemical performance of three-component, layered-layered-spinel electrodes through parallel ***Processing***, ***characterization***, and ***modeling*** efforts

Milestones (FY16)

- Characterize bulk and surface properties of structurally-integrated electrode materials using DOE's User Facilities at Argonne (APS, EMC and ALCF) and facilities elsewhere, e.g., the neutron spallation source at Oak Ridge National Laboratory (SNS) and the NUANCE characterization center (Northwestern University). **Achieved. Project on-going.**
- Use complementary theoretical approaches to further the understanding of the structural and electrochemical properties of layered-spinel electrodes and protective surface layers. **Achieved. Project on-going**
- Analysis, interpretation, and dissemination of collected data for publication and presentation. **Achieved. Project on-going.**

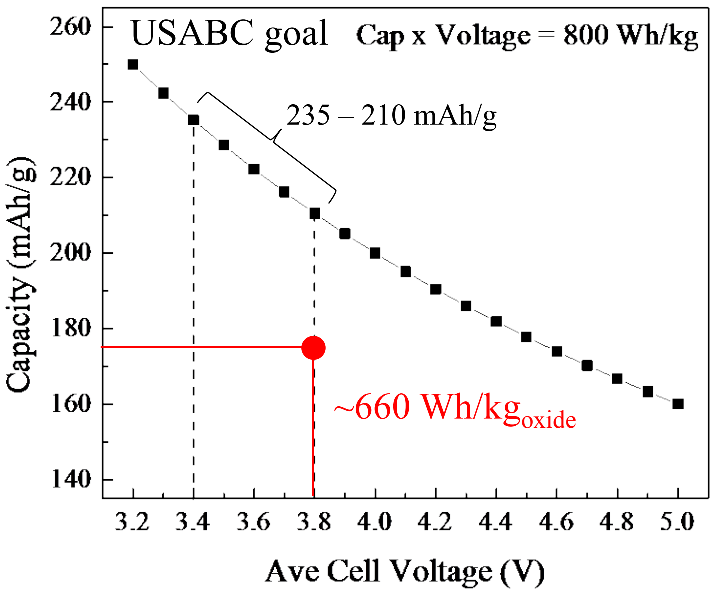
Approach

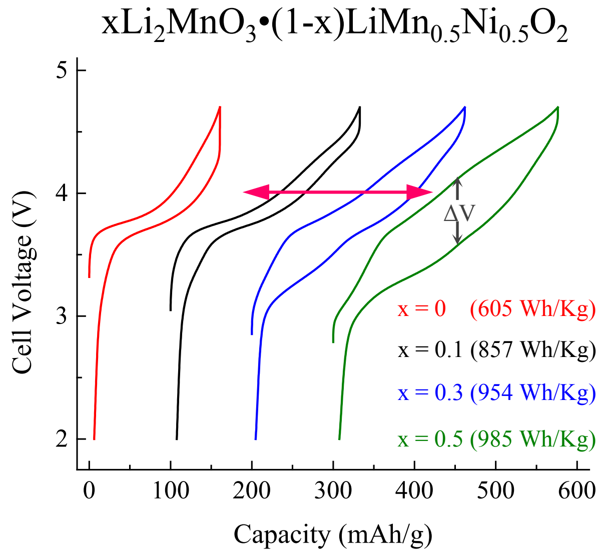
- A wide array of characterization techniques including X-ray and neutron diffraction, X-ray absorption, high resolution transmission electron microscopy, nuclear magnetic resonance spectroscopy, and theory are being brought together to focus on challenging experimental problems. Combined, these resources promise an unparalleled look into the structural, electrochemical and chemical mechanisms at play in novel, complex electrode/electrolyte systems being explored at Argonne National Laboratory.

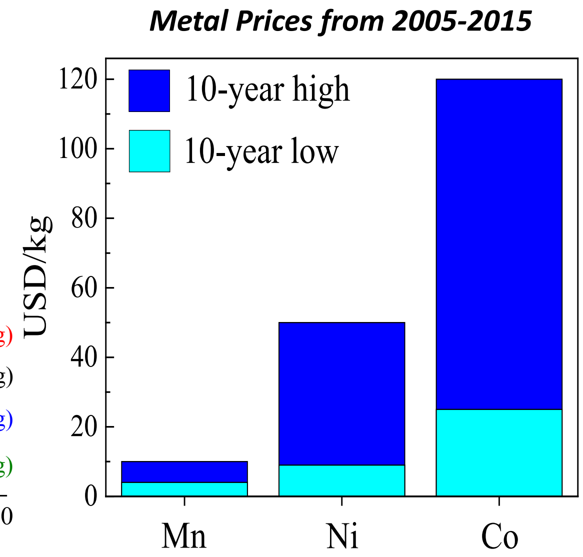
- Selective characterization and modeling collaborations within and outside of Argonne

- *Particle processing and the associated electrochemical properties are critical aspects of characterization and will be used to inform efforts.*

Relevance: High-Capacity, Low Cost Materials



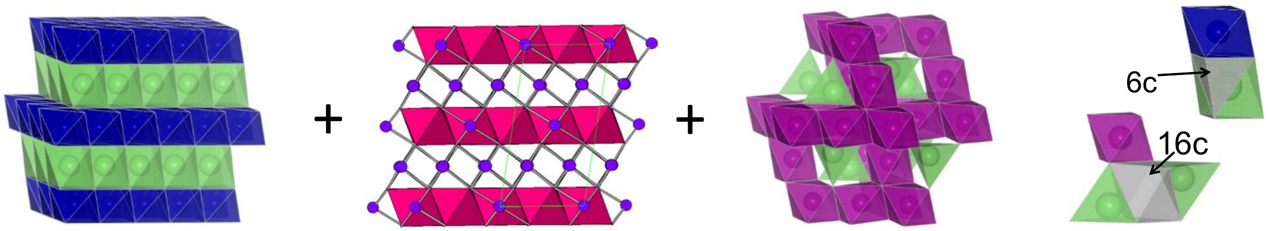




- Next-Gen cathodes require specific oxide-energy densities of ≥800 Wh/kg$_{oxide}$
- SOA lithium-ion cathodes are limited to ~700 Wh/kg$_{oxide}$ (●) with a current trend towards increasingly high nickel contents → cost/safety
- Lithium- and ***manganese-rich*** cathodes can deliver considerably higher energies
- ***Manganese-rich*** cathodes are being developed as viable alternatives to nickel-rich systems

Relevance: Understanding Complex Materials

Integrated structures offer
Unique design space



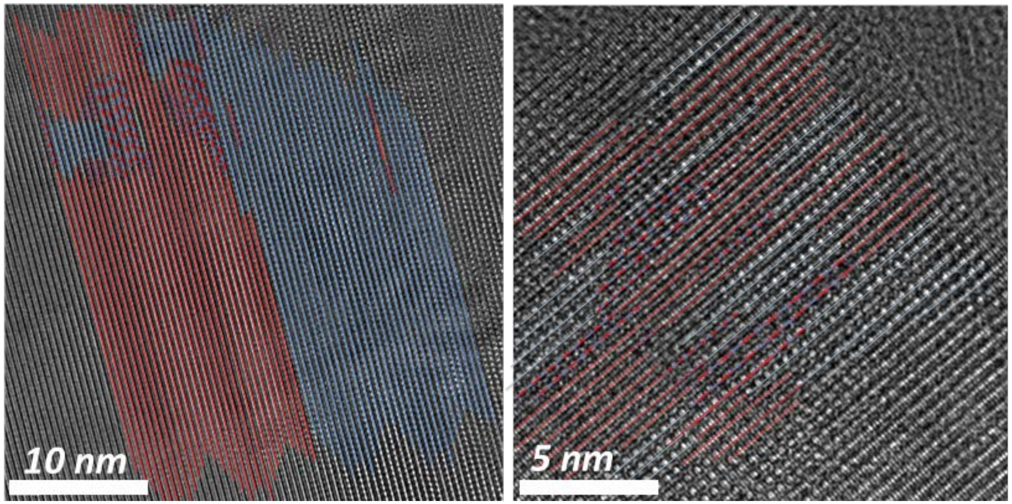
Stable performance
Low capacity

Low cost, high capacity
Not stable

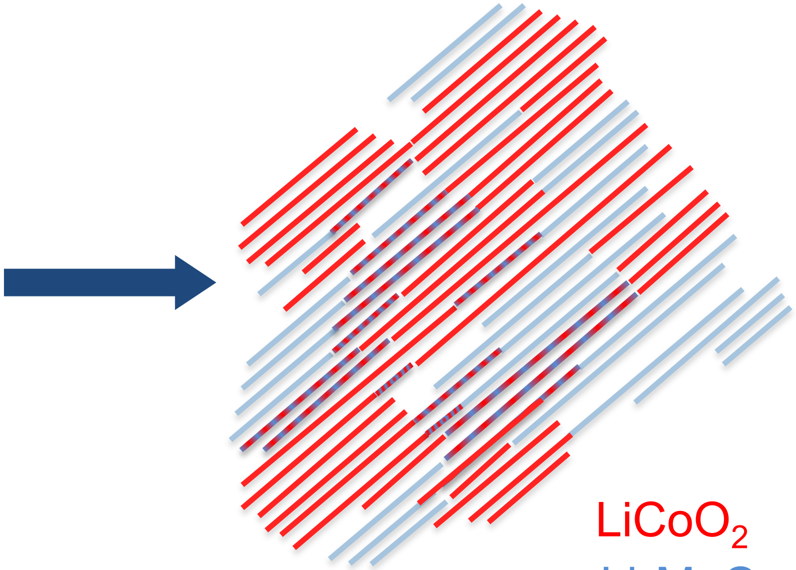
High power
Low capacity

Unique pathways
& TM migration

$0.5Li_2MnO_3 \bullet 0.5LiCoO_2$



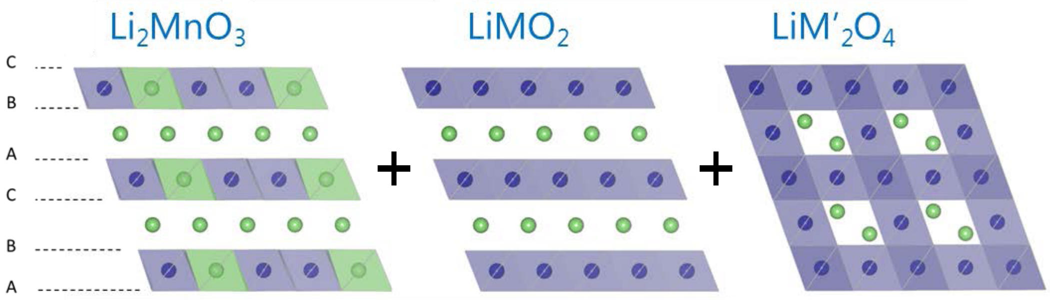
D. Miller, J.G. Wen

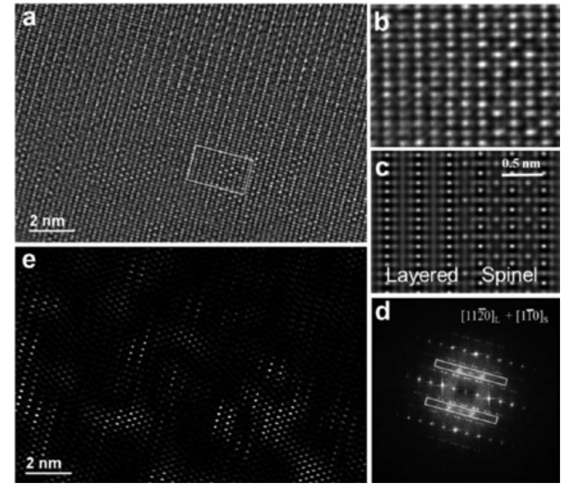


However, even “simple” compositions lead to complex local structures and electrochemical properties

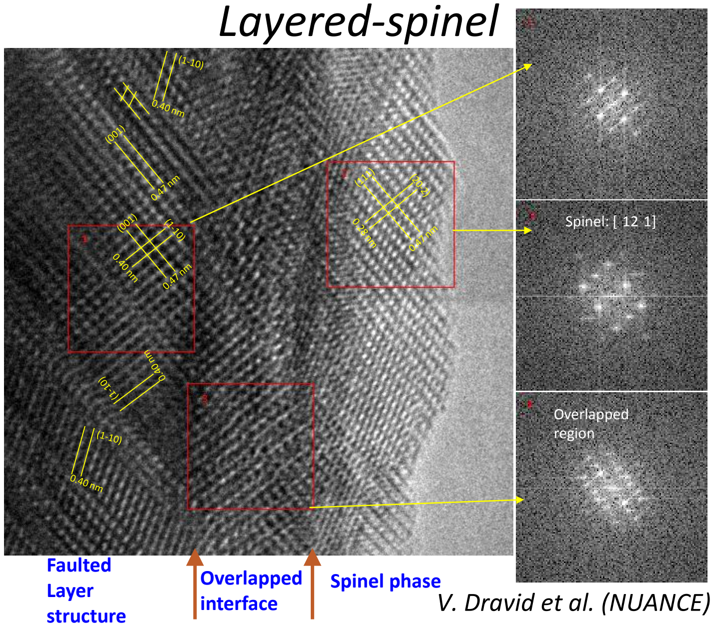
Relevance: Understanding Complex Materials

Extend concept of integrated structures to 'layered-layered-spinel' (LLS) systems





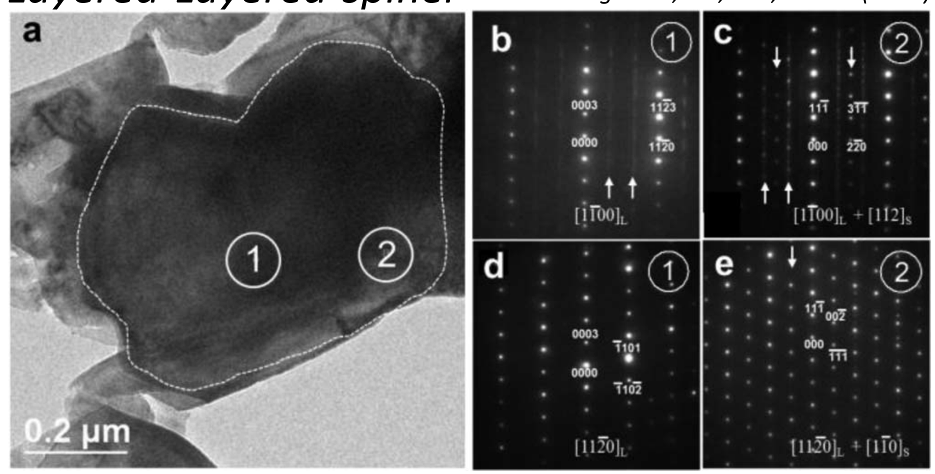
Layered-spinel



V. Dravid et al. (NUANCE)

Layered-Layered-spinel

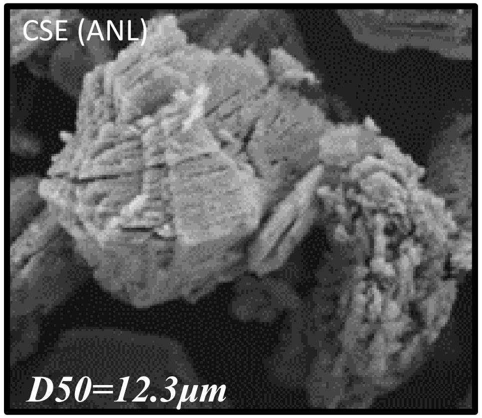
Long et al., JES, 161, A2160 (2014)



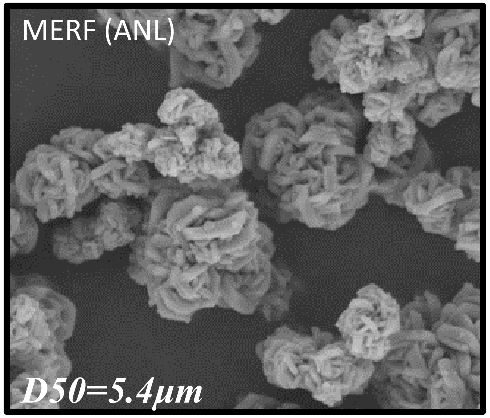
Nanoscale inhomogeneity and local ordering often missed but critical → combination of processing/characterization necessary to understand across length-scales

Progress: Processing

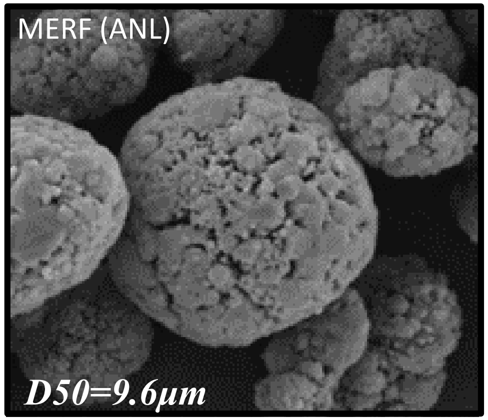
Bench-scale oxalate



CSTR hydroxide



CSTR carbonate

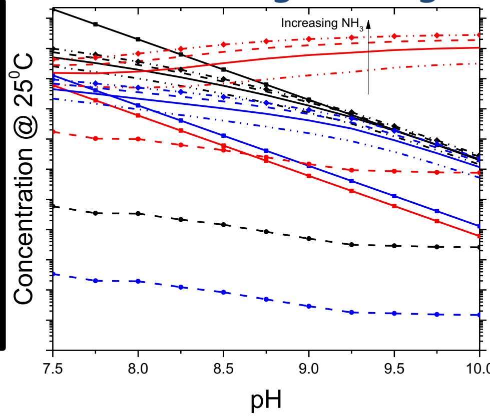


- Processing routes explored from bench-scale to 4L CSTR at CSE to 20L CSTR reactor at ANL's MERF facility: oxalate, hydroxide, carbonate precursors considered
- Even particles showing similar ICP, XRD, and particle size can have dramatically different morphologies, porosities, and tap densities and affect electrochemical performance
- Morphology and porosity also important when considering surface treatments
- Carbonate precursors have, so far, led to highest tap densities and best performance for Mn-rich LLS particles

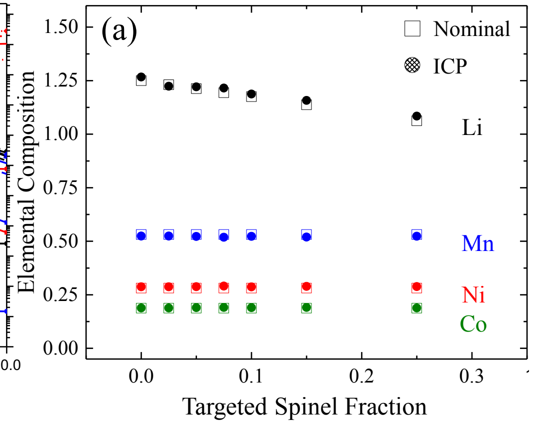
Progress: Processing

4L CSTR reactor

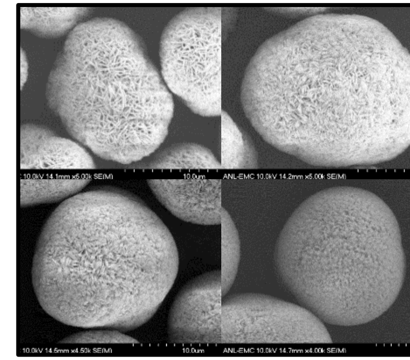
Process Engineering



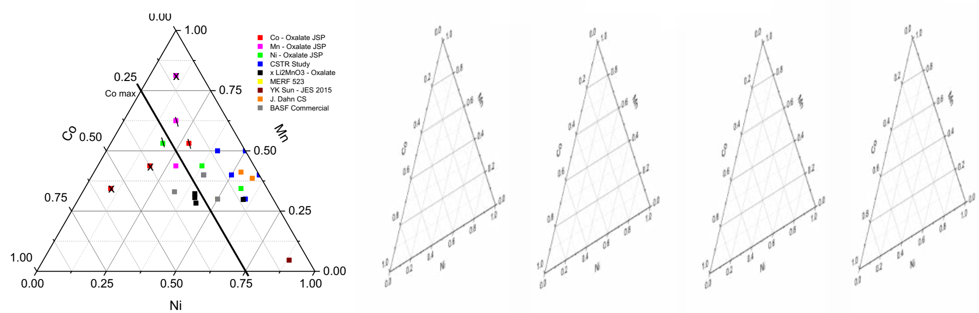
Elemental analysis (ICP)



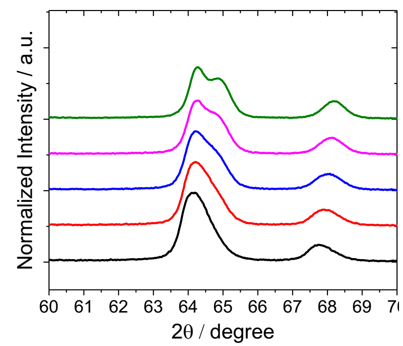
High quality results

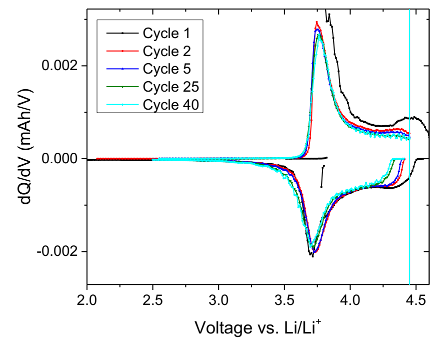


TM content → *Li content* → *structure* → *Echem* →



Compositional Studies





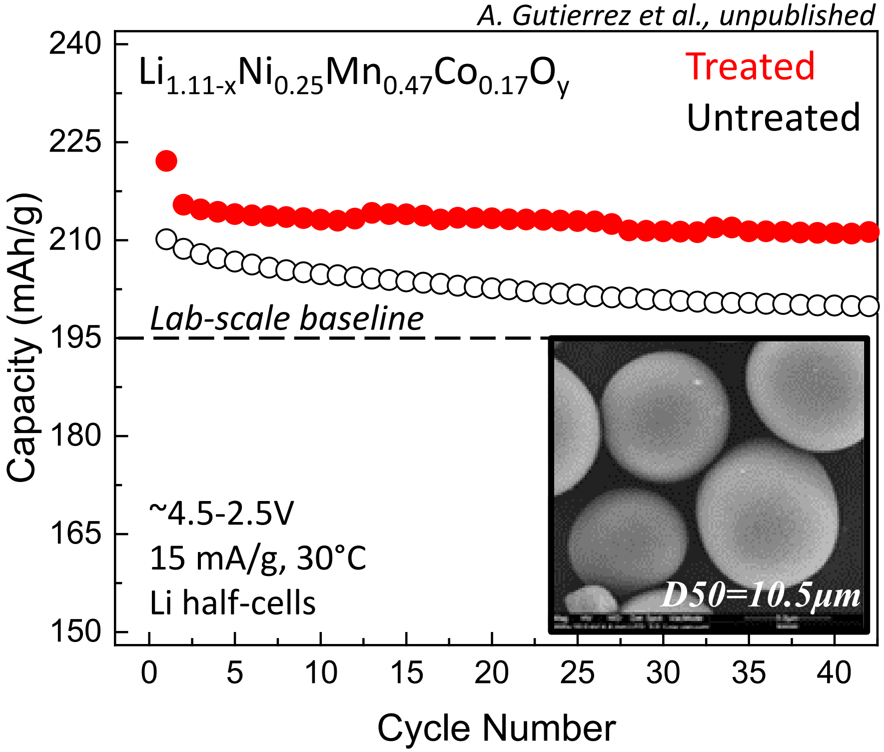
Intensive processing studies have resulted in a high-quality, *baseline*, LLS cathode material

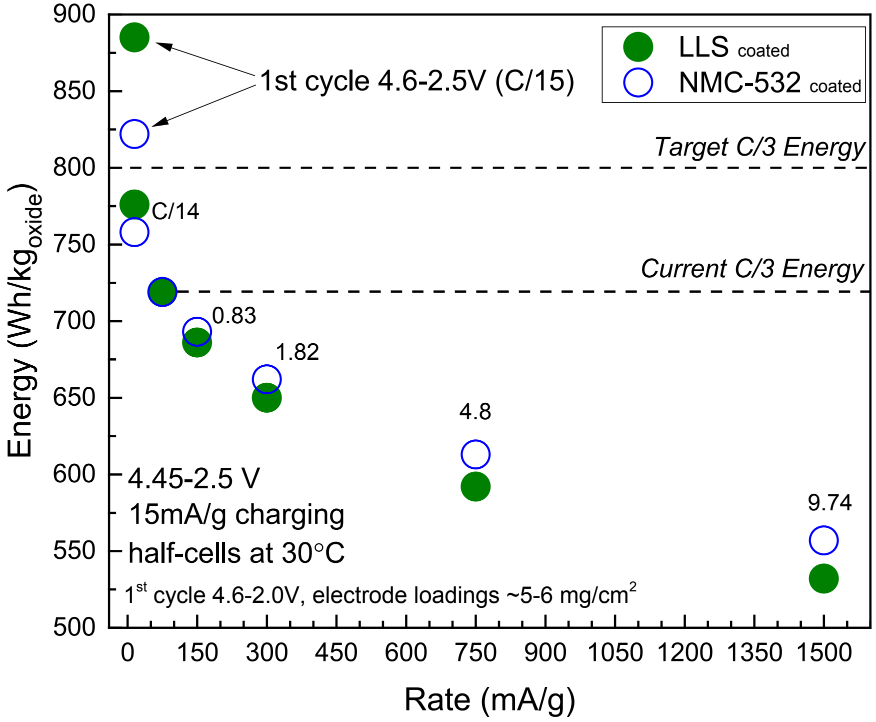
- >200 mAh/g
- >2.0g/cc tap densities
- Scaled up (~1kg) MERF
- >50% Mn
- ~750 Wh/kg$_{\text{oxide (\textasciitilde C/10)}}$
- Under eval. by industry

B. Yonemoto et al., unpublished

Progress: Processing

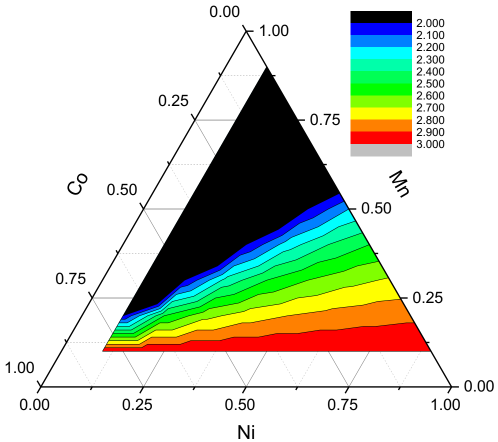
See also ES049

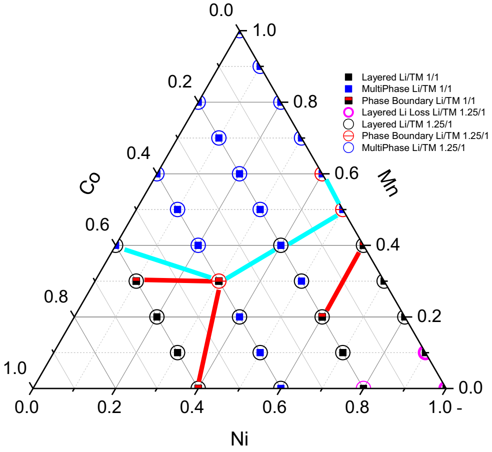




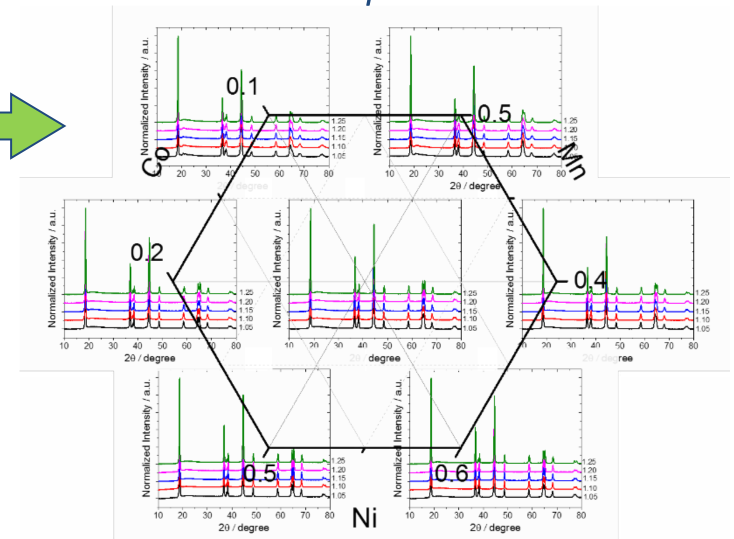
- LLS achieves ~215 mAh/g between 4.5-2.5V vs. Li/Li^+ (~4.4V vs. graphite)
- Early results on surface treatments (Al_2O_3, Li_3PO_4, $Li_{2.9}Ni_{0.05}PO_4$, AlW_xF_y…) show promise
- Rate and energy are comparable to Ni-rich, NMC-532 (*lab-scale electrodes, Li half-cells*)
- Further improvements still necessary (*voltage fade, rate, full-cell testing*)

Progress: Processing, *On-going*

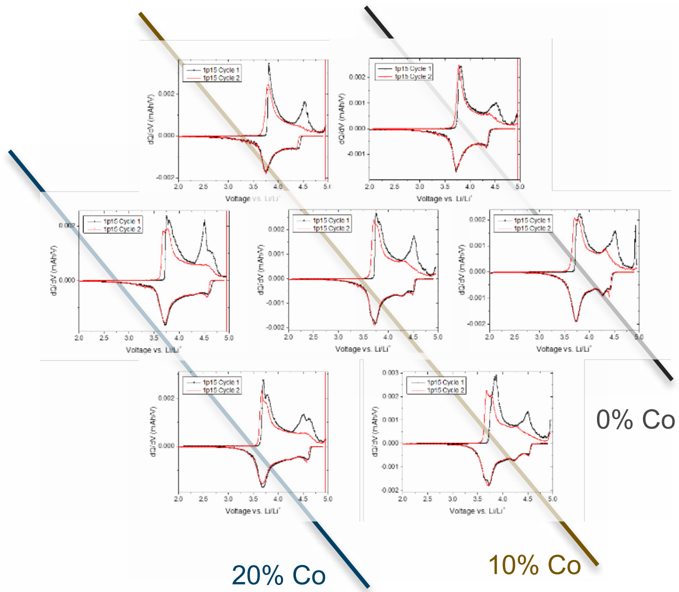




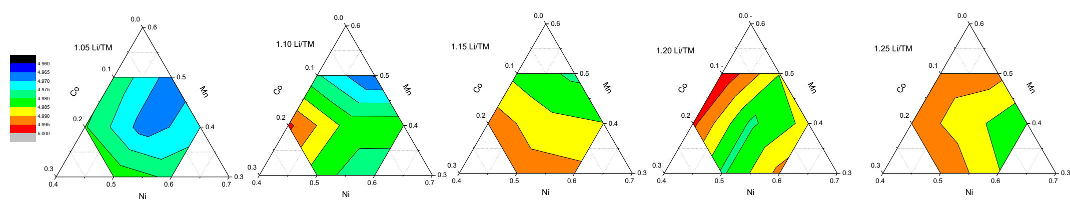
XRD comparisons



Standard cycling comparisons



Performance vs. specific elemental content



- Select screening based on literature and ANL results
- 40+ layered-layered-(spinel) compositions selected
- Initial characterization and cycling complete

B. Yonemoto et al., unpublished

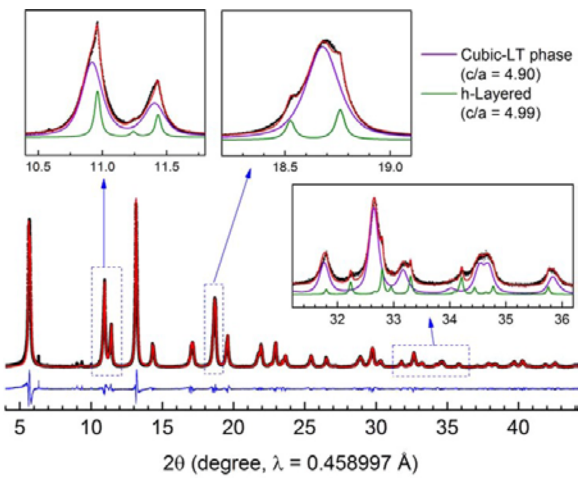
Progress: Characterization

see also ES049 2016

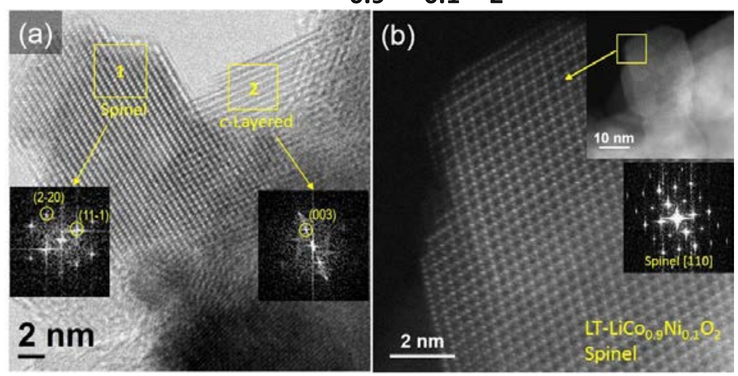
Integration of Co-based, lithiated, $Li_{2-x}[Co_{2-2y}Ni_{2y}]O_4$ spinel component

- Close-packed structure, rock-salt stoichiometry → compatible with xLi_2MnO_3•$(1-x)LiMO_2$
- Low propensity for $Co^{3+/4+}$ migration → stability
- Lithium extraction occurs at higher voltages (~3.6V) than manganese spinel (~2.9V)

LT-$LiCoO_2$

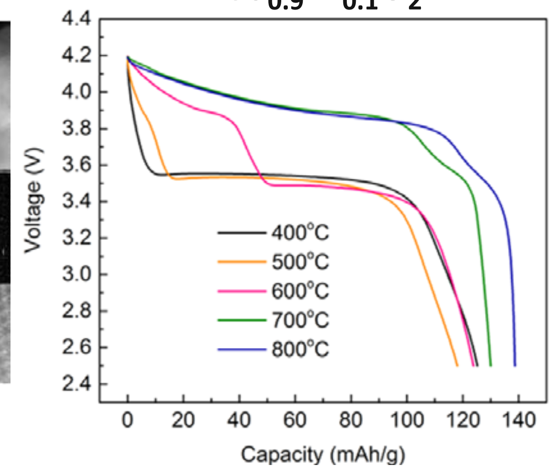


LT-$LiCo_{0.9}Ni_{0.1}O_2$



Lee et al., Appl. Mater. Interfaces, 8, 27720 (2016)

$LiCo_{0.9}Ni_{0.1}O_2$

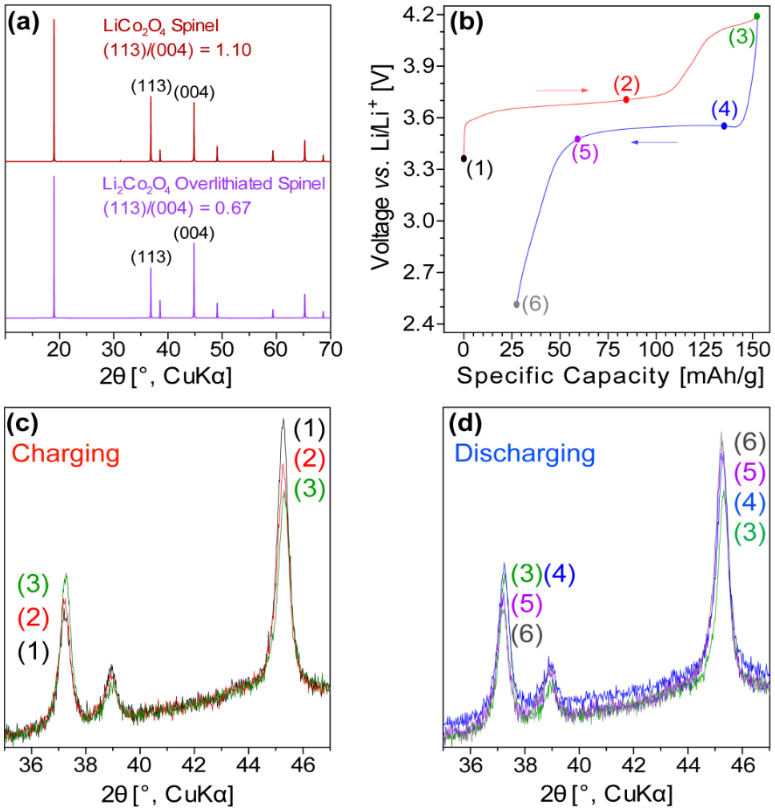


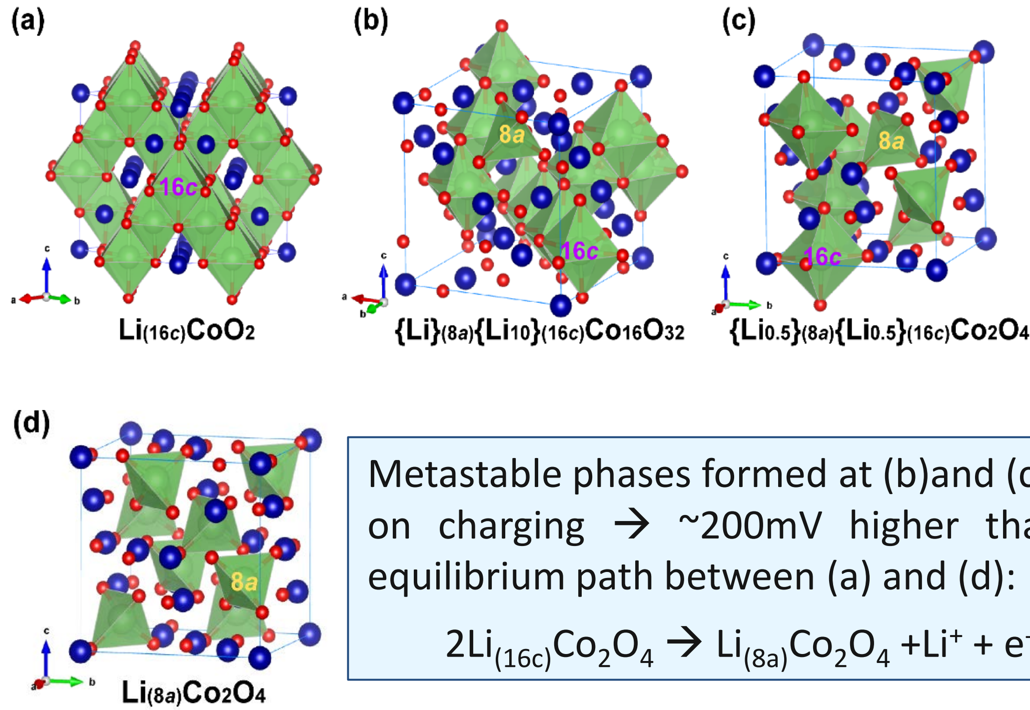
- LT-$LiCo_{1-x}Ni_xO_2$ (~400°C) consists primarily of lithiated-spinel, structurally integrated with a "defect" layered phase in which the cation distribution is intermediate between layered/spinel
- Ni substitution is limited but, importantly, promotes the formation of spinel and suppresses the spinel-to-layered transition at elevated annealing temperatures
- HT-$LiCo_{1-x}Ni_xO_2$ integrated structures can be "controlled" → possible integration in LLS composites

Progress: Modeling

see also ES049 2016

S. Kim, C. Wolverton (NU)



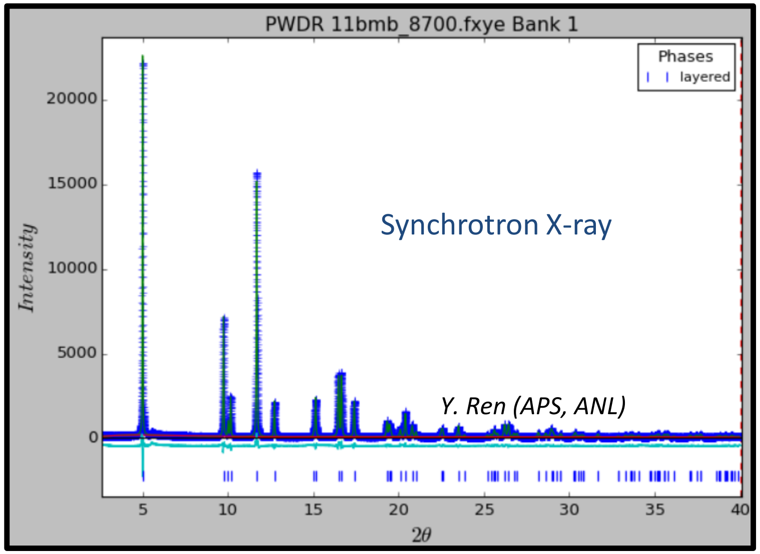


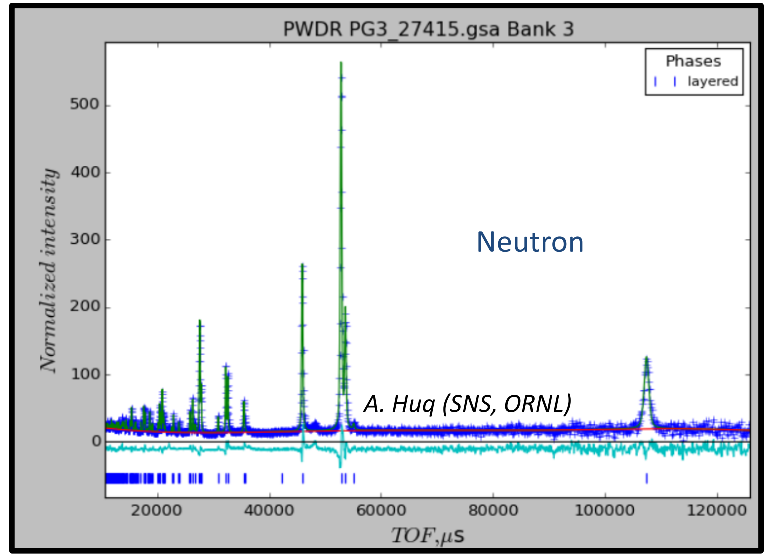
Metastable phases formed at (b) and (c) on charging → ~200mV higher than equilibrium path between (a) and (d):

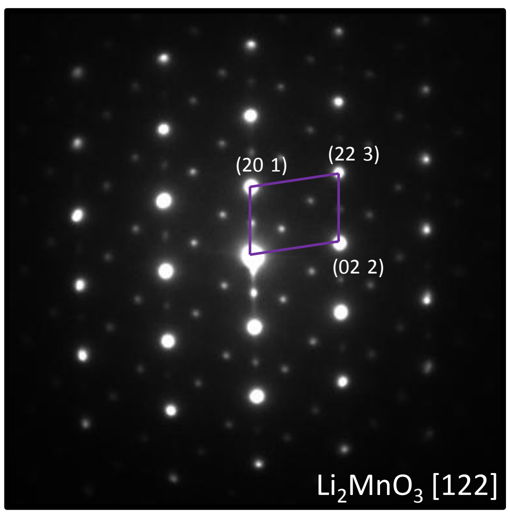
$$2Li_{(16c)}Co_2O_4 \rightarrow Li_{(8a)}Co_2O_4 + Li^+ + e^-$$

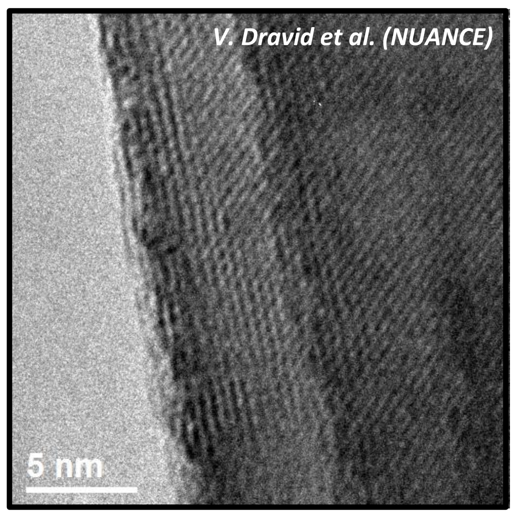
- Occupancy of Li_{Oct} and Li_{tet} can be monitored by *I(311)/I(400)* in HR-XRD (left)
- DFT calculations in agreement with Li occupancies as well as the observed hysteresis
- Hysteresis may result from non-equilibrium pathway through metastable states

Progress: Integration of Spinel









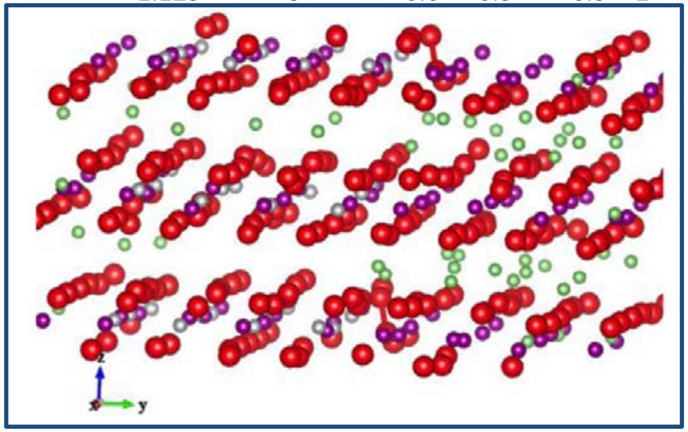
- Ongoing analysis of LLS as a function of Li and Co content
- Combined HR-XRD/Neutron
- Complementary microscopy of surface and bulk
- Electrochemistry

Ongoing characterization to better understand “spinel” as a function of Li/co content and synthesis

Progress: Modeling

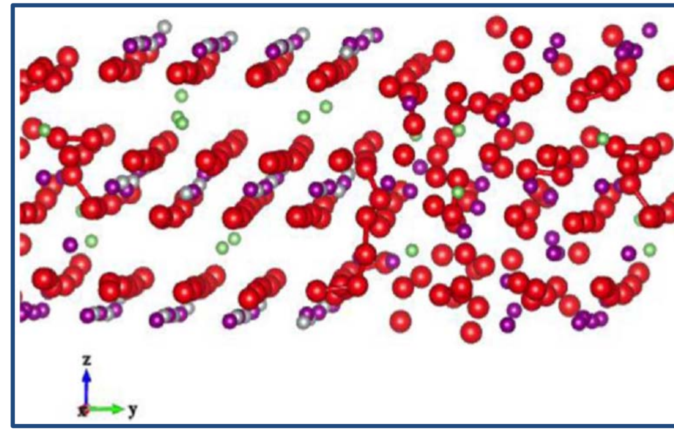
Iddir, Bareño, Benedek, JES, 163, A1784 (2016)
Iddir, Benedek, J. Phys. Chem. C. (2017)

~0.4$Li_{1.125}MnO_3$•0.6$Li_{0.0}Ni_{0.5}Mn_{0.5}O_2$



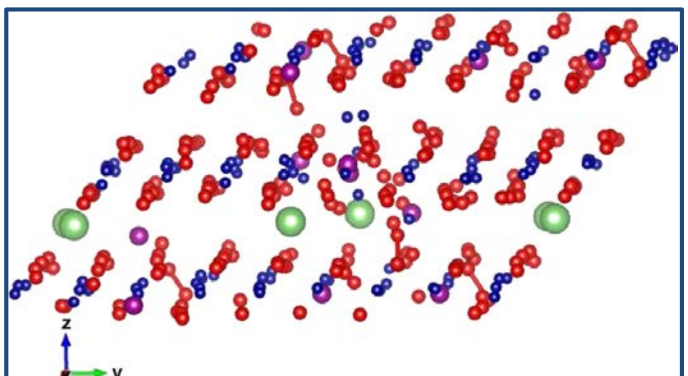
Oxygen lattice stays intact up to ~½ Li removal from Li-layer (Li_{Li}) of Li_2MnO_{33}

~0.4$Li_{0.50}MnO_3$•0.6$Li_{0.00}Ni_{0.5}Mn_{0.5}O_2$



Removal of all Li-layer Li leads to O migration and ***O-O pairing*** → opens pathways for ***Mn migration***

~0.1$Li_{0.50}MnO_3$•0.9$Li_{0.00}CoO_2$



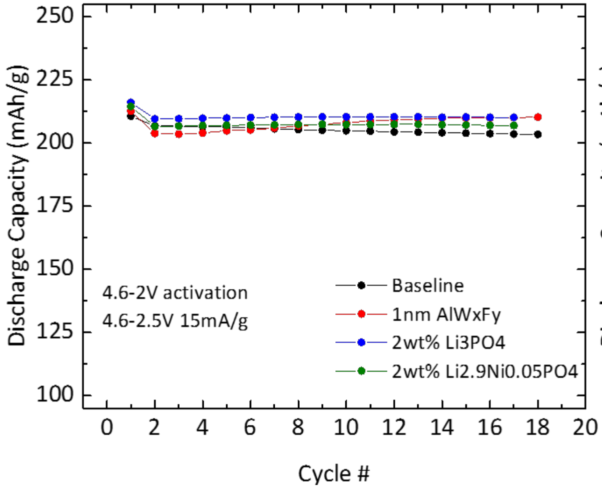
O-O pairs preferentially formed in Li- Mn-rich domains → in agreement with experiment

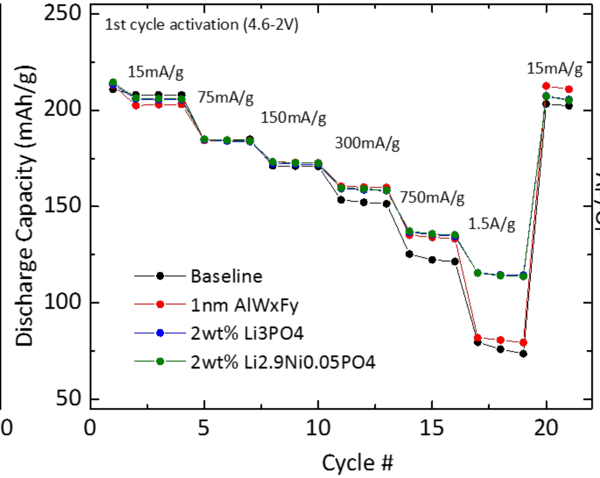
See Croy et al., JES, 161, A318 (2014)

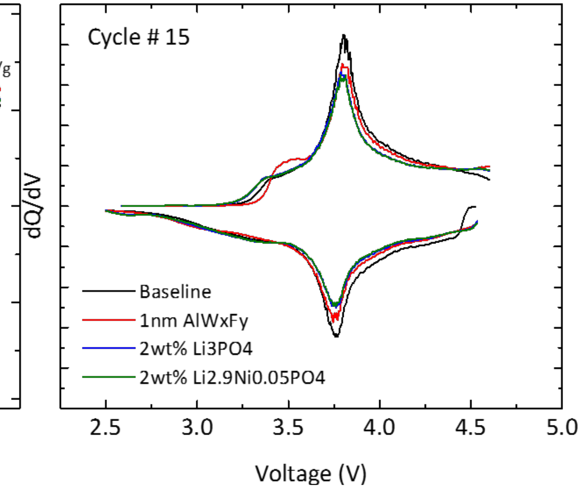
- Simulations show that bulk oxygen lattice is stable up to ~50% Li removal from Li-layers of Li_2MnO_3 component
- Mn migration is correlated with O-O pairing
- Surface stability is essentially zero, and any Li extraction leads to more instabilities
- Suggests that some capacity from Li_2MnO_3 could be utilized if surfaces can be stabilized

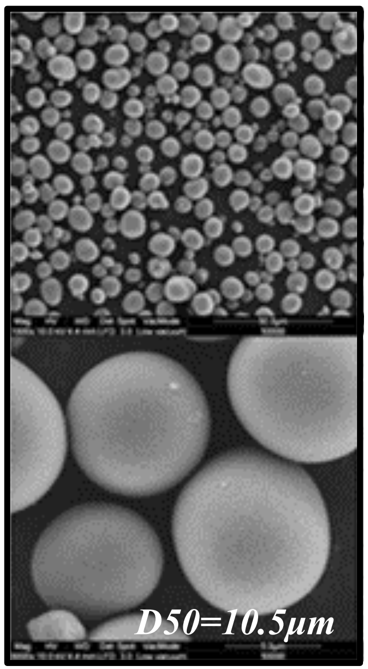
Progress: Surfaces

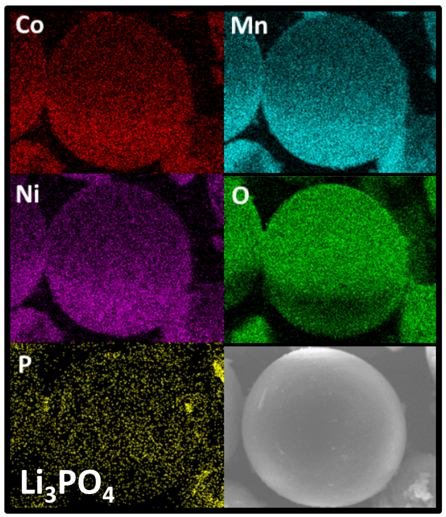
Croy et al., J. Power Sources, 334, 213 (2016)

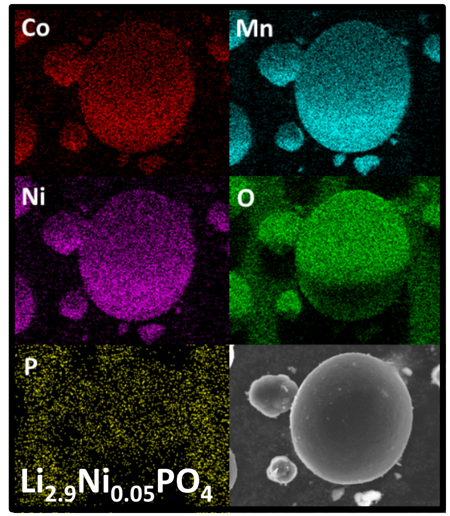


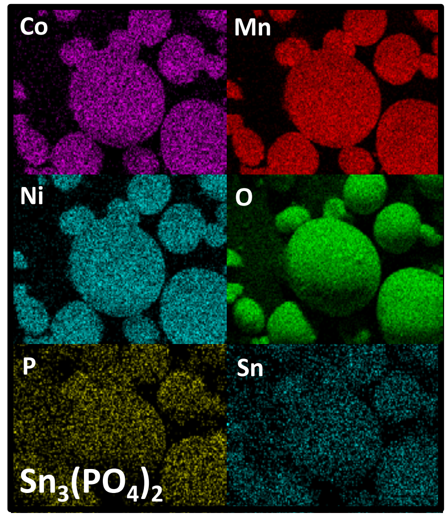










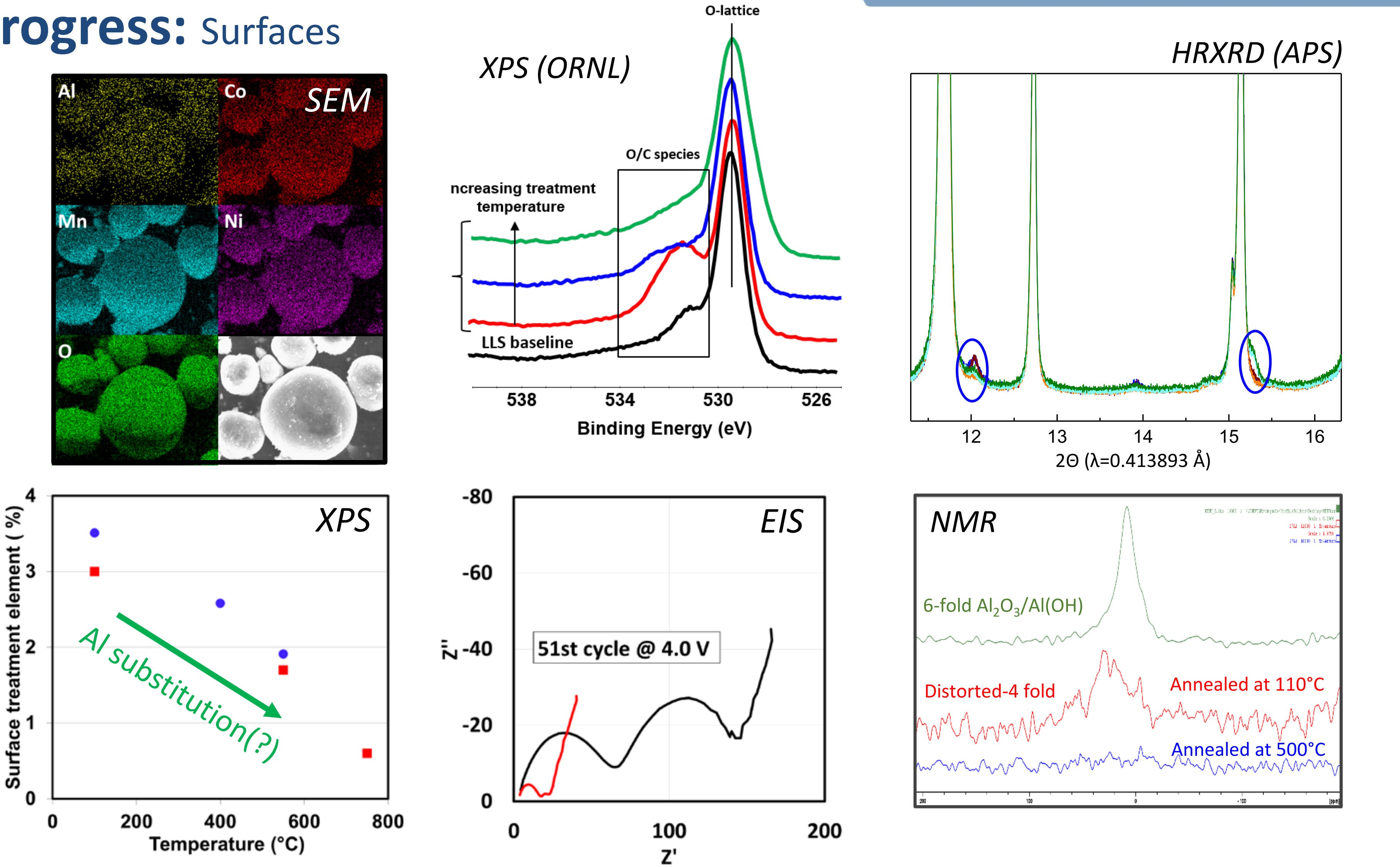


A. Gutierrez et al., unpublished

- Surface-treated powders/electrodes show good performance and improved rate
- A variety of materials beneficial, $Li_{2.9}Ni_{0.05}PO_4$ shows best, high-rate performance

Surface stabilization is critical for all cathode materials, characterization ongoing

Progress: Surfaces



- Low-temp Al (~110°C) treatments proved *effective* – low impedance rise, high capacity retention
- Increasing temperature led to an apparent increase in the incorporation of Al into cathode particles and poor electrochemical performance – ***different behavior compared to NMC***

Future Work FY17/18

- Promising results encourage further exploration of Mn-rich, layered-layered-spinel electrodes including processing and synthesis conditions

- 40+ new compositions have been synthesized and are currently being characterized and screened for specific elemental-structural-electrochemical properties

- Characterization efforts will complement synthesis efforts (see ES049) in order to understand the possibilities and electrochemical effects of incorporating Co-rich, spinel, $Li_{2-x}[Co_{2-2y}Ni_y]O_4$ components

- Characterization of robust surface structures will be explored and complemented with theory/simulation on Li- and Mn-rich surface structures protected with a variety of materials – including new designs not yet reported

- Characterization of LLS electrode systems exposed to various electrochemical conditions in full-cell (vs. graphite anodes) configurations will be examined to better ascertain practical performance and the efficacy of various surface treatments

Any proposed future work is subject to change based on funding levels

Summary

- Many collaborations have been established and include expertise in XAS, HRXRD, HRTEM, NMR, ND, XPS, Theory, and Processing and span 4 ANL divisions, 3 Nat. Labs, 2 Univ. groups, Rutherford Lab (U.K.), and outside industrial partners
- Particle processing and the associated electrochemical performance are important aspects of characterization studies and must be part of the analyses
- Ongoing processing studies have led to Mn-rich, LLS cathode powders giving high capacity (>210 mAh/g), energy (>700 Wh/kg @ C/3), and rate with promising stability
- $Li_{2-x}[Co_{2-2y}Ni_y]O_4$ spinel end-members have been studied and understood via complementary HRTEM, HRXRD, processing, electrochemistry, and theory
- Calculation/simulations show that surface protection is essential for Li- and Mn-rich cathode materials and may lead to enhanced stability of the oxygen sub-lattice in the bulk of particles under certain conditions
- A variety of surface treatments have proven beneficial for LLS particles including new and novel materials: $Li_{2.9}Ni_{0.05}O_4$, AlW_xF_y, $Sn_3(PO_4)_2$

Acknowledgments

Support for this work from the BMR Program, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Tien Duong, David Howell